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A process for the preparation of a poly-1-olefin by polymerizing a 1-olefin of the formula $R^1CH=CH_2$ in which R^1 is hydrogen or an alkyl radical having 1 to 10 carbon atoms, in suspension, in solution or in the gas phase, at a temperature of 20 to 200°C and under a pressure of 0.5 to 50 bar, in the presence of a catalyst composed of the reaction product of a magnesium alcoholate with a transition metal compound (component a) and an organometallic compound of a metal of group I, II or III of the periodic table (component b), which comprises carrying out the polymerization in the presence of a catalyst in which the component a has been prepared by reacting a transition metal compound of titanium, zirconium, vanadium or chromium with a gel-like dispersion of the magnesium alcoholate in an inert, saturated hydrocarbon.

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COMPLETE SPECIFICATION

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PROCESS FOR THE PREPARATION OF A POLY-1-OLEFIN

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Description

Process for the preparation of a poly-1-olefin

The invention relates to a process for the preparation of a poly-1-olefin using a catalyst based on a gel-like magnesium alcoholate dispersion.

5 Solids can be prepared from magnesium alcoholates $Mg(OR^1)(OR^2)$ or "complex" magnesium alcoholates by reaction with compounds of titanium, zirconium, vanadium or chromium, and these solids, together with organo-metallic compounds of the 1st to 3rd main groups of the
10 periodic table, produce excellent catalysts for olefin polymerization.

A process is known for the polymerization of α -olefins in the presence of a mixed catalyst in which the component
15 A has been prepared by reacting magnesium alcoholates with tetravalent halogen-containing titanium compounds (cf. US 3,644,318). The magnesium alcoholates are employed in the form in which they are available commercially. The polymers obtainable by this process have a narrow molecular weight distribution.

20 A process is also known for the preparation of a Ziegler catalyst, in which a dissolved magnesium alcoholate is reacted with a halogen-containing Ti or V compound and a transition metal alcoholate (cf. EP 319,173). The catalyst particles thus formed are spherical and have an
25 average particle size of 10 to 70 μm .

Finally, it is known to use (cf. EP 223,011) as the transition metal component a product from the reaction of a tetravalent, halogen-containing titanium compound with
30 a magnesium alcoholate containing at least 40 % by weight of particles having a diameter smaller than 63 μm . A magnesium alcoholate of this particle size is obtained,

inter alia, by grinding a commercial product in a ball mill. The magnesium alcoholate is employed in the form of a suspension in an inert hydrocarbon. However, the known catalysts are still not satisfactory.

5 It has been found that catalysts having a high to very high activity and enabling the particle size distribution of the polymer to be controlled are obtained if the magnesium alcoholate is employed in the form of a gel-like dispersion.

10 The invention therefore relates to a process for the preparation of a poly-1-olefin by polymerizing a 1-olefin of the formula $R^1CH=CH_2$ in which R^1 is hydrogen or an alkyl radical having 1 to 10 carbon atoms, in suspension, in solution or in the gas phase, at a temperature of 20
15 to 200°C and under a pressure of 0.5 to 50 bar, in the presence of a catalyst composed of the reaction product of a magnesium alcoholate with a transition metal compound (component a) and an organometallic compound of a metal of group I, II or III of the periodic table
20 (component b), which comprises carrying out the polymerization in the presence of a catalyst in which the component a has been prepared by reacting a transition metal compound of titanium, zirconium, vanadium or chromium with a gel-like dispersion of the magnesium
25 alcoholate in an inert, saturated hydrocarbon.

The invention also relates to the catalyst employed in this process.

A commercially available magnesium alcoholate is used for the preparation of the component a.

30 This magnesium alcoholate can be a "simple" magnesium alcoholate of the formula $Mg(OR^1)(OR^2)$ in which R^1 and R^2 are identical or different and are each an alkyl radical having 1 to 6 carbon atoms. Examples are $Mg(OC_2H_5)_2$, $Mg(OiC_3H_7)_2$, $Mg(OnC_4H_9)_2$, $Mg(OCH_3)(OC_2H_5)$ and

$\text{Mg}(\text{OC}_2\text{H}_5)(\text{OnC}_3\text{H}_7)$. It is also possible to use a "simple" magnesium alcoholate of the formula $\text{Mg}(\text{OR})_n\text{X}_m$ in which X is halogen, $(\text{SO}_4)_{1/2}$, OH, $(\text{CO}_3)_{1/2}$, $(\text{PO}_4)_{1/3}$ or Cl, R has the abovementioned meaning of R^1 or R^2 and $n + m$ is 2.

5 It is also possible, however, to employ a "complex" magnesium alcoholate. A "complex" magnesium alcoholate signifies a magnesium alcoholate which, as well as magnesium, contains at least one metal of the 1st to 4th main groups of the periodic table. The following are
10 examples of complex magnesium alcoholates of this type:

$[\text{Mg}(\text{Oic}_3\text{H}_7)_4]\text{Li}_2$; $[\text{Al}_2(\text{Oic}_3\text{H}_7)_8]\text{Mg}$; $[\text{Si}(\text{OC}_2\text{H}_5)_6]\text{Mg}$;
 $[\text{Mg}(\text{OC}_2\text{H}_5)_3]\text{Na}$; $[\text{Al}_2(\text{Oic}_4\text{H}_9)_8]\text{Mg}$; $[\text{Al}_2(\text{O-secC}_4\text{H}_9)_6(\text{OC}_2\text{H}_5)_2]\text{Mg}$.
The preparation of the complex magnesium alcoholates (alkoxo salts) is effected by known methods. The following
15 ing examples of the preparation may be mentioned:

1. Two metal alcoholates are allowed to act on one another in a suitable solvent, for example $2\text{Al}(\text{OR})_3 + \text{Mg}(\text{OR})_2 \rightarrow [\text{Al}_2(\text{OR})_8]\text{Mg}$

20 2. Magnesium is dissolved in an alcoholic solution of a metal alcoholate;
 $2\text{LiOR} + \text{Mg} + 2 \text{ROH} \rightarrow [\text{Mg}(\text{OR})_4]\text{Li}_2 + \text{H}_2$

3. Two metals are dissolved in alcohol at the same time,
 $8 \text{ROH} + \text{Mg} + 2 \text{Al} \rightarrow [\text{Al}_2(\text{OR})_8]\text{Mg} + 4 \text{H}_2$.

25 It is preferable to use a simple magnesium alcoholate, in particular $\text{Mg}(\text{OC}_2\text{H}_5)_2$, $\text{Mg}(\text{OnC}_3\text{H}_7)_2$ or $\text{Mg}(\text{Oic}_3\text{H}_7)_2$. The magnesium alcoholate is employed in the pure form.

In general, commercially available $\text{Mg}(\text{OC}_2\text{H}_5)_2$ has the following specification:

30	Mg content	21-22	% by weight
	Total of $\text{Mg}(\text{OH})_2$ and MgCO_3	≤ 1	% by weight
	$\text{C}_2\text{H}_5\text{OH}$ content	< 0.3	% by weight.

The average particle diameter is 500 μm . 90 % of the particles have a particle diameter within the range from 200 to 1200 μm .

5 The magnesium alcoholate is suspended in an inert, saturated hydrocarbon. The suspension is converted into a gel-like magnesium alcoholate dispersion under a protective gas (Ar or N_2) in a reactor by means of a high-speed disperser (for example "Ultra-Turrax" or "Dispax, IKA-Maschinenbau Janke & Kunkel GmbH).

10 This dispersion differs from the suspension in two essential characteristics. It is substantially more viscous than the suspension and is gel-like, and, compared with the suspended magnesium alcoholate, the dispersed magnesium alcoholate settles out very much more slowly and to a far lesser extent (after a few hours, 15 volume of the supernatant hydrocarbon approx. 80 % by volume in the case of suspended magnesium alcoholate and approx. 10 % by volume in the case of dispersed magnesium alcoholate, at the same content (131 g/l dm^3)).

20 The dispersed magnesium alcoholate can also be prepared by mechanical comminution with glass spheres (\varnothing 1 cm) in a round-bottomed flask, the contents of the flask being agitated by means of a two-bladed stirrer. However, this process is very time-consuming.

25 A suitable inert, saturated hydrocarbon is an aliphatic or cycloaliphatic hydrocarbon, such as butane, pentane, hexane, heptane, isooctane, cyclohexane or methylcyclohexane, and also an aromatic hydrocarbon, such as toluene or xylene; it is also possible to use hydrogenated diesel 30 oil or gasoline fractions which have been carefully freed from oxygen, sulfur compounds and moisture.

The gel-like dispersion is then reacted, in one stage or in several stages, with a Ti compound (TiCl_4 , Ti(OR) , and others), Zr compound (Zr(OR) , and others), V compound

(VCl_4 , VOCl_3 , and others) or Cr compound (CrO_2Cl_2 and others).

5 In this reaction the magnesium alcoholate is reacted with the transition metal compound at a temperature of 50 to 100°C , preferably 60 to 90°C , in the presence of an inert hydrocarbon and with stirring. 0.9 to 5 mol of transition metal compound are employed per 1 mol of magnesium alcoholate, preferably 1.4 to 3.5 mol of transition metal compound per 1 mol of magnesium alcoholate.

10 The reaction time is 0.5 to 8 hours, preferably 2 to 6 hours.

This gives a solid insoluble in hydrocarbon and containing magnesium and transition metal, which is named as component a.

15 The preparation of the polymerization catalyst to be used in accordance with the invention is effected by combining the component a and an organometallic compound of a metal of group I, II or III of the periodic table (component b).

20 The component a in the form of a suspension can be reacted, without further treatment, with the component b; it can, however, also be first isolated as a solid, stored and resuspended for subsequent use.

25 It is preferable to use organoaluminum compounds as the component b. Suitable organoaluminum compounds are chlorine-containing organoaluminum compounds, the dialkylaluminum monochlorides of the formula R_2^3AlCl or alkylaluminum sesquichloride of the formula $\text{R}_3^3\text{Al}_2\text{Cl}_2$, in which R^3 is an alkyl radical having 1 to 16 carbon atoms. $(\text{C}_2\text{H}_5)_2\text{AlCl}$, $(i\text{C}_4\text{H}_9)_2\text{AlCl}$ and $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_2$ may be mentioned as examples. It is also possible to use mixtures of these
30 compounds.

It is particularly preferable to employ chlorine-free compounds as organoaluminum compounds. Suitable for this purpose are, on the one hand, the reaction products of aluminum trialkyls or aluminum dialkylhydrides having hydrocarbon radicals having 1 to 6 carbon atoms, preferably $\text{Al}(\text{iC}_4\text{H}_9)_3$ or $\text{Al}(\text{iC}_4\text{H}_9)_2\text{H}$, with diolefins containing 4 to 20 carbon atoms, preferably isoprene. Isoprenylaluminum may be mentioned as an example.

On the other hand, suitable chlorine-free organoaluminum compounds of this type are aluminum trialkyls AlR_3^3 or aluminum dialkylhydrides of the formula AlR_2^3H in which R^3 is an alkyl radical having 1 to 16 carbon atoms. $\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{Al}(\text{C}_2\text{H}_5)_2\text{H}$, $\text{Al}(\text{C}_3\text{H}_7)_3$, $\text{Al}(\text{C}_3\text{H}_7)_2\text{H}$, $\text{Al}(\text{iC}_4\text{H}_9)_3$, $\text{Al}(\text{iC}_4\text{H}_9)_2\text{H}$, $\text{Al}(\text{C}_8\text{H}_{17})_3$, $\text{Al}(\text{C}_{12}\text{H}_{25})_3$, $\text{Al}(\text{C}_2\text{H}_5)(\text{C}_{12}\text{H}_{25})_2$ and $\text{Al}(\text{iC}_4\text{H}_9)(\text{C}_{12}\text{H}_{25})_2$ are examples.

It is also possible to employ mixtures of organometallic compounds of metals of group I, II or III of the periodic table, particularly mixtures of different organoaluminum compounds.

The following mixtures may be mentioned as examples: $\text{Al}(\text{C}_2\text{H}_5)_3$ and $\text{Al}(\text{iC}_4\text{H}_9)_3$, $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and $\text{Al}(\text{C}_8\text{H}_{17})_3$, $\text{Al}(\text{C}_2\text{H}_5)_3$ and $\text{Al}(\text{C}_8\text{H}_{17})_3$, $\text{Al}(\text{C}_4\text{H}_9)_2\text{H}$ and $\text{Al}(\text{C}_8\text{H}_{17})_3$, $\text{Al}(\text{iC}_4\text{H}_9)_3$ and $\text{Al}(\text{C}_8\text{H}_{17})_3$, $\text{Al}(\text{C}_2\text{H}_5)_3$ and $\text{Al}(\text{C}_{12}\text{H}_{25})_3$, $\text{Al}(\text{iC}_4\text{H}_9)_3$ and $\text{Al}(\text{C}_{12}\text{H}_{25})_3$, $\text{Al}(\text{C}_2\text{H}_5)_3$ and $\text{Al}(\text{C}_{16}\text{H}_{33})_3$, $\text{Al}(\text{C}_3\text{H}_7)_3$ and $\text{Al}(\text{C}_{18}\text{H}_{37})_2(\text{iC}_4\text{H}_9)$, $\text{Al}(\text{C}_2\text{H}_5)_3$ and isoprenylaluminum (the reaction product of isoprene with $\text{Al}(\text{iC}_4\text{H}_9)_3$ or $\text{Al}(\text{iC}_4\text{H}_9)_2\text{H}$).

Mixing of the component a and the component b can be carried out before polymerization, in a stirred vessel at a temperature of -30°C to 150°C , preferably -10 to 120°C . It is also possible to combine the two components without further treatment in the polymerization vessel at a temperature of 20 to 200°C . It is also possible, however, to add the component b in two stages, by preactivating, before the polymerization reaction, the component a with

part of the component b at a temperature of -30°C to 150°C , and adding the remainder of the component b in the polymerization reactor at a temperature of 20 to 200°C .

5 The polymerization catalyst to be used in accordance with the invention is employed for the polymerization of 1-olefins of the formula $\text{R}'\text{-CH=CH}_2$, in which R' is a hydrogen atom or an alkyl radical having 1 to 10 carbon atoms, for example ethylene, propylene, but-1-ene, hex-1-ene, 4-methylpent-1-ene or oct-1-ene.

10 It is preferable to polymerize ethylene on its own or as a mixture of at least 50 % by weight of ethylene and not more than 50 % by weight of another 1-olefin of the above formula.

15 In particular, ethylene on its own or a mixture of at least 90 % by weight of ethylene and not more than 10 % by weight of another 1-olefin of the above formula is polymerized.

20 The polymerization is carried out in a known manner in solution, in suspension or in the gas phase, continuously or batchwise, in one or more stages and at a temperature of 20 to 200°C , preferably 50 to 150°C . The pressure is 0.5 to 50 bar. Polymerization is preferably effected in the pressure range from 5 to 30 bar which is of particular industrial interest.

25 In this reaction the component a is used in a concentration, relative to transition metal, of 0.0001 to 1, preferably 0.001 to 0.5, mmol of transition metal per dm^3 of dispersing agent. The organometallic compound is used in a concentration of 0.1 to 5 mmol, preferably 0.5 to 30 4 mmol per dm^3 of dispersing agent. In principle, however, higher concentrations are also possible.

The suspension polymerization is carried out in an inert dispersing agent which is customary for the Ziegler low

pressure process, for example in an aliphatic or cyclo-
aliphatic hydrocarbon; examples of these which may be
mentioned are butane, pentane, hexane, heptane, iso-
octane, cyclohexane or methylcyclohexane. It is also
5 possible to use gasoline fractions or hydrogenated diesel
oil fractions which have been carefully freed from
oxygen, sulfur compounds and moisture.

The gas phase polymerization can be carried out without
further treatment or after prepolymerization of the
10 catalyst in a suspension process.

The molecular weight of the polymer is controlled in a
known manner, it being preferable to use hydrogen for
this purpose.

As a result of the high activity of the catalyst used,
15 the process according to the invention gives polymers
having a very low content of transition metal and halo-
gen, and, therefore, extremely good values in the color
stability and corrosion test.

The process according to the invention also makes it
20 possible to prepare the catalysts in such a way that the
particle size distribution and, to a certain extent, also
the particle shape of the polymer powder formed can
thereby be adjusted.

In general, an improved particle morphology, a high
25 average particle diameter (d_{50} values), a narrow particle
size distribution, no coarse and fine fractions and high
catalyst productivities are obtained. The bulk densities
are comparable with those of the state of the art.

Thus it is possible, when using these gel-like dis-
30 persions of magnesium alcoholates, to influence the
morphological properties of the polymer powder, which
affords advantages for an industrial process (filtration
of the polymer powder is simpler, the residual contents

of dispersing agent are lower and, as a result, the energy expended in drying is lower, the transport of the polymer powder in the plant is simpler, its pourability is better and the proportion of fines in the cyclones of the driers is lower). The high catalyst productivity results in lower residual contents of catalyst in the product.

The following examples are intended to illustrate the invention.

10 A hydrogenated diesel oil fraction having a boiling range from 130 to 170°C was used in the examples for preparation of the catalyst and for polymerization.

The Mg:Ti:Cl ratios used for characterizing the catalysts were determined by customary analytical methods.

15 The titanium content by weight of the catalyst used to calculate the catalyst productivity CP (see tables) was determined as follows:

20 A definite volume of the catalyst suspension was removed by pipette. The catalyst was hydrolyzed with sulfuric acid and the titanium content was determined by known methods.

Result: titanium content (mmol) per unit volume (cm³).

25 A second sample of the suspension was removed by pipette, the suspending agent was removed in vacuo and the solid was weighed.

Result: solid (g) per unit volume (cm³). The ratio of these gives mmol of Ti/g of catalyst.

Example 1

30 1.2 mol of Mg(OC₂H₅)₂ ($\hat{=}$ 137 g) were suspended in 1.0 dm³ (1) of diesel oil. The suspension was converted into a dispersion under a protective gas (Ar or N₂), in order to exclude moisture and air (O₂), in a cylindrical glass

vessel by means of a high-speed disperser (time approx. 3 hours). The dispersion had a gel-like consistency. The difference between the suspension and the dispersion could be seen without difficulty.

5 **Comparison Example A**

Preparation of the catalyst component a using an $\text{Mg}(\text{OC}_2\text{H}_5)_2$ suspension.

57 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ were suspended in 0.5 dm³ (l) of diesel oil (a hydrogenated gasoline fraction having a boiling range of 120-140°C) in a 2 dm³ stirred vessel equipped with a reflux condenser, a 2-b lade paddle stirrer and blanketing with protective gas (Ar). The suspension was brought to 85°C. The stirrer speed was set at 350 r.p.m. (optimum stirrer speed when using suspended Mg alcoholate; if the stirrer speed is set lower, inhomogeneous, unusable catalysts are formed). 0.15 mol of TiCl_4 in 350 cm³ of diesel oil were metered in in the course of 4 hours. The resulting suspension was then heated at 110°C for 1 hour. A mixture of 0.2 mol of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ and 0.2 mol of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ in 400 cm³ of diesel oil was then metered in in the course of 2 hours. The temperature was then kept at 110°C for a further 2 hours. This concluded the preparation of the catalyst component a. The suspension of solids was allowed to cool to room temperature. The molar ratio was: $\text{Mg}:\text{Ti}:\text{Cl} \approx 1:0.3:2.4$. This catalyst component a was given the operation number 2.1.

Example 2

A catalyst was prepared by the process of Comparison Example A, using the gel-like dispersion of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ prepared in accordance with Example 1 (in this case there is no particle size distribution; the average particle diameter is $\leq 1 \mu\text{m}$). The molar ratio was approximately: $\text{Mg}:\text{Ti}:\text{Cl} \approx 1:0.3:2.4$. This catalyst component was given the operation number 2.2.

Example 3

57 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ were dispersed in 0.5 dm^3 of diesel oil in a 2 dm^3 stirred vessel equipped with a reflux condenser, a stirrer and blanketing with protective gas (Ar). The gel-like dispersion was brought to 85°C . The stirrer speed was adjusted to 150 rpm. 0.15 mol of TiCl_4 in 350 cm^3 of diesel oil were metered in in the course of 4 hours.

The subsequent reaction of the resulting suspension with $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ was carried out as described in Comparison Example A.

The molar ratio was approximately: $\text{Mg}:\text{Ti}:\text{Cl} \approx 1:0.3:2.4$. This catalyst component was given the operation number 2.3.

Example 4

Preparation was performed as in Example 3, but the reaction was carried out at 85°C at a stirrer speed of 75 rpm. The molar ratio was: $\text{Mg}:\text{Ti}:\text{Cl} = 1:0.3:2$. This catalyst component a was given the operation number 2.4.

If a magnesium ethylate suspension as in Comparison Example A is used, and the stirrer speed is altered (cf. Examples 2 to 4), unusable catalysts are obtained, because the suspended magnesium ethylate does not react uniformly and thus a homogeneous catalyst suspension is not formed. If the stirrer speed is increased ($> 350 \text{ r.p.m.}$), homogeneous catalysts are obtained, but these form a very fine polymer powder and are thus again not optimum.

Comparison Example B

Comparison Example A was repeated using an $\text{Mg}(\text{OC}_2\text{H}_5)_2$ suspension obtained from finely divided $\text{Mg}(\text{OC}_2\text{H}_5)_2$ ($d_{50} \approx 6 \mu\text{m}$). The molar ratio $\text{Mg}:\text{Ti}:\text{Cl}$ was about $1:0.3:2.4$. This catalyst component a was given the operation number 2.5.

The suspension had a milky cloudiness, whereas the $\text{Mg}(\text{OC}_2\text{H}_5)_2$ dispersion was only slightly cloudy (Tyndall phenomenon).

Example 5

5 Polymerization tests using catalysts of operation number 2.1 to 2.4 and 2.5.

The polymerization tests were carried out batchwise in a 200 dm^3 reactor. This reactor was equipped with an im-
10 peller stirrer and a flow breaker. The temperature in the reactor was measured and was kept constant by automatic means. The polymerization temperature was $85 \pm 1^\circ\text{C}$. The polymerization reaction was carried out in the following manner:

15 100 dm^3 of diesel oil were run into the reactor, which was blanketed with N_2 , and were heated to 85°C . The co-catalyst ($\text{Al}(\text{C}_2\text{H}_5)_3$) was then added under N_2 at such a rate that the concentration of co-catalyst in the reactor was 0.14 mmol/dm^3 . The catalyst component a was then added, the catalyst content in the diesel oil being $\approx 1 \text{ mmol}/\text{dm}^3$.
20 The catalyst content was quoted in g-atoms of titanium. The titanium content in the suspension of solids was determined colorimetrically.

The pressure in the reactor was repeatedly pressurized to 8 bar with H_2 (hydrogen) and depressurized, in order to
25 remove the nitrogen completely from the reactor (the procedure was checked by measuring the H_2 concentration in the gas space of the reactor, which finally indicated 95 % by volume). The polymerization was initiated by opening the ethylene inlet. During the whole poly-
30 merization time ethylene was fed in at a rate of 7.0 kg/hour. The content of ethylene and hydrogen in the gas space of the reactor was measured continuously and the volume ratios were kept constant by suitably metering in hydrogen (% by volume of $\text{H}_2 = 50$; % by volume of $\text{C}_2\text{H}_4 = 45$).
35

The polymerization was terminated when the total pressure had reached 9.5 bar. The contents of the reactor were drained off onto a filter. The polymer, which contained diesel oil, was dried for several hours in a stream of nitrogen. The polymerization results are shown in Table 1.

The particle size distribution of the polymer powder, which is shown in Table 2 (as specified in DIN 66 144), shows the great increase in the d_{50} value at a parallel displacement of the curves. This means that the particle size distribution remains the same, the increase is only in the median particle diameter. Therefore the fine fractions ($< 100 \mu\text{m}$) decrease considerably, which is particularly advantageous.

It can also be seen that the catalyst productivity increases greatly with a simultaneous increase in the melt flow index values at the same hydrogen content in the gas space of the reactor.

All the products obtained had a narrow molecular weight distribution as measured by GPC. The M_w/M_n values were between 5 and 6. These were therefore injection molding products.

Comparison Example C

57 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ were suspended in 0.5 dm^3 (l) of diesel oil (a hydrogenated gasoline fraction having a boiling range of $120\text{--}140^\circ\text{C}$) in a 2 dm^3 stirred vessel equipped with a reflux condenser, a 2-bladed paddle stirrer and blanketing with protective gas (Ar). The suspension was brought to 85°C . The stirrer speed was set at 350 r.p.m. 1.0 mol of TiCl_4 (undiluted) was added dropwise in the course of 4 hours. After the TiCl_4 had been added the batch was allowed to react further for 1 hour under the conditions indicated above. The suspension of solids formed was washed several times with fresh diesel oil at 60°C until the titanium content in the suspending agent

was less than 10 mmol. When this had been achieved the suspension of solids was allowed to cool to room temperature.

The molar ratio Mg:Ti:Cl was approximately: 1:0.085:2.1.

5 This catalyst component a was given the operation number 3.1.

Example 6

10 The preparation of the catalyst component a was carried out similarly to Comparison Example C, using a gel-like $\text{Mg}(\text{OC}_2\text{H}_5)_2$ dispersion, but with the difference that the stirrer speed was 75 r.p.m. The molar ratio Mg:Ti:Cl was approximately: 1:0.17:2.4. This catalyst component a was given the operation number 3.2.

Example 7

15 Polymerization tests using the catalysts of operation number 3.1 and 3.2 were carried out as described in Example 5. The amounts of catalyst and co-catalyst and the composition in the gas space of the reactor (% by volume of H_2 = 36; % by volume of C_2H_4 = 60) were
20 different. The results are collated in Table 3. The sieve analysis data are shown in Table 4.

Comparison Example D

25 57 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ were suspended in 0.5 dm³ of diesel oil (a hydrogenated gasoline fraction having a boiling range of 140-170°C) in a 2 dm³ stirred vessel equipped with a reflux condenser, a 2-bladed paddle stirrer and blanket-
ing with protective gas (Ar). The suspension was brought to 120°C. The stirrer speed was adjusted to 350 r.p.m. 0.65 mol of TiCl_4 (undiluted TiCl_4) was added uniformly
30 in the course of 5 hours. The batch was then stirred at 120°C for 60 hours. It was then cooled to 70°C and the solid was washed with fresh diesel oil until the titanium content in the diesel oil (dissolved titanium compound) was < 5 mmol/dm³. In this method ethyl chloride was split
35 off at 120°C. This catalyst component a was given the

operation number 4.1. Mg:Ti:Cl = 1:1.3:3.6.

Comparison Example E

Comparison Example D was repeated, using a finely divided suspension of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ ($d_{50} \approx 6 \mu\text{m}$). This catalyst component a was given the operation number 4.2. Mg:Ti:Cl \approx 1:1.3:3.6.

Example 8

Preparation of the catalyst component a

Comparison Example D was repeated, using a dispersion of $\text{Mg}(\text{OC}_2\text{H}_5)_2$. The catalyst component a was given the operation number 4.3. Mg:Ti:Cl \approx 1:1.3:4.

Example 9

Polymerization tests were carried out with the catalyst components a of operation numbers 4.1 - 4.3. The co-catalyst was different. Isoprenylaluminum (commercial product) was employed in this case. It was necessary to alter the amounts of catalyst component a and co-catalyst, and also the composition in the gas space of the reactor (% by volume of $\text{H}_2 = 55$; % by volume of $\text{C}_2\text{H}_4 = 40$). The results are collated in Table 4. All the products obtained had a broad distribution of molecular weights as measured by GPC. The M_w/M_n values were between 10 and 15. These were therefore extrusion grades.

It can be seen that the catalyst component a prepared from the gel-like dispersion differs advantageously in median particle size (d_{50} value) and in catalyst productivity from the catalyst components a which were prepared from a suspension of coarse or finely divided magnesium ethylate.

Comparison Example F

57 g of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ were suspended in 0.5 dm^3 of diesel oil, at a stirrer speed of 350 r.p.m., in a 2 dm^3 stirred vessel equipped with a reflux condenser, a 2-bladed

paddle stirrer and blanketing with protective gas (Ar). The suspension was brought to 85°C. 1.25 mol of TiCl_4 were added dropwise in the course of 5.5 hours. When the addition of TiCl_4 was complete, the batch was stirred at 85°C for 1 hour. The solid was washed with diesel oil at 65°C until the Ti content in the diesel oil was < 5 mmol/dm³. Sufficient diesel oil was added to reach the original level of filling in the stirred vessel. 60 mmol of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ were then added and the temperature was raised over 20 hours, with stirring. This catalyst component a was given the operation number 5.1. The Mg:Ti:Cl ratio was approximately 1:0.135:2.15.

Comparison Example G

Comparison Example F was repeated, using a finely divided suspension of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ ($d_{50} \approx 6 \mu\text{m}$).

The catalyst component a was given the operation number 5.2. The Mg:Ti:Cl ratio was approximately 1:0.14:2.15.

Example 10

The catalyst was prepared in accordance with Comparison Example F, using a dispersion of $\text{Mg}(\text{OC}_2\text{H}_5)_2$. The stirrer speed was 350 r.p.m. The catalyst component a was given the operation number 5.3. The Mg:Ti:Cl ratio was approximately 1:0.20:2.3.

Example 11

Example 10 was repeated, using a dispersion of $\text{Mg}(\text{OC}_2\text{H}_5)_2$. However, the stirrer speed was 75 r.p.m. The catalyst component a was given the operation number 5.4. The Mg:Ti:Cl ratio was approximately 1:0.28:2.4.

Example 12

Polymerization tests were carried out in accordance with Example 5, using the catalyst components a 5.1 to 5.4. Triisobutylaluminum (commercial product) was employed as the co-catalyst. It was necessary to alter the amounts of the catalyst component a and the co-catalyst, and also

the composition in the gas space of the reactor (% by volume of H_2 = 40; % by volume of C_2H_4 = 55). The results are collated in Table 4. These catalysts produce a molecular weight distribution, as measured by GPC, with M_w/M_n values of 7-10.

Example 13

Copolymerization tests were carried out batchwise in a 200 dm³ reactor using the catalyst component a 4.3. This reactor was equipped with an impeller stirrer and a flow breaker. The temperature was controlled automatically. The temperature of the tests was 85°C ± 1°C. The polymerization was carried out in accordance with Example 5. Initial charge: 100 dm³ of diesel oil; co-catalyst: isoprenylaluminum; co-catalyst concentration 1.2 mmol/dm³. % by volume of H_2 in the gas space as measured by gas chromatography: 40 % by volume. Ethylene feed rate: 5 kg/hour, reaction time: 4 hours.

The polymerization was initiated by opening the ethylene inlet. The comonomer was added 5 minutes later (see Table 5). In order to keep the comonomer content in the gas space (measured by gas chromatography) constant, comonomer was continuously metered in subsequently (see Table 5). As the time progressed, the pressure in the reactor increased. The pressures after 4 hours are also shown in Table 5. The table contains further data concerning catalyst productivity (CP), melt flow index (MFI) as specified in DIN 53 735 and density (d) as specified in DIN 53 479.

Table 1 Polymerization tests: 200 dm³ reactor;85°C, 100 dm³ of diesel oil, 7 kg/hour of ethylene,

Pressure (maximum) 9.5 bar, 50 % by volume of hydrogen in the gas space

Catalyst	n _c ¹⁾ [mmol]	n _{AlR₃} ²⁾ [mmol]	CP ³⁾ [kg/g]	MFI 190/5 ⁴⁾ [g/10']	BD ⁵⁾ [g/cm ³]	d ₅₀ ⁶⁾ [μm]
Op. No. 2.1	1	14	22 ⁷⁾	9.5	0.37	150
Op. No. 2.5	1.1	14	18 ⁷⁾	10.0	0.36	140
Op. No. 2.2	0.9	14	50 ⁸⁾	16	0.37	260
Op. No. 2.3	0.9	14	55 ⁸⁾	17	0.34	440
Op. No. 2.4	0.9	14	50 ⁸⁾	16	0.31	480

¹⁾ Amount of catalyst in mmol of transition metal (Ti) compound²⁾ Amount of co-catalyst (Al(C₂H₅)₃)³⁾ Catalyst productivity (kg of PE/g of catalyst)⁴⁾ Melt flow index as specified in DIN 53 735⁵⁾ Bulk density as specified in DIN 53 468⁶⁾ d₅₀ value from logarithmic standard distribution as specified in DIN 66 144⁷⁾ Ti content of the catalyst: 1.47 mmol/g⁸⁾ Ti content of the catalyst: 1.73 mmol/g

Table 2 Particle size distribution analysis of the PE powders
Original weight: 100 g; final weight in g on the sieve indicated

Component a
Operational No.

Sieve	2.1	2.5	2.2	2.3	2.4
1000 μm	-	-	-	4.0	10.3
800 μm	-	-	-	4.6	8.8
600 μm	-	-	1.0	4.8	10.4
500 μm	-	-	3.5	16.4	15.9
400 μm	-	-	4.3	29.5	24.4
300 μm	2.6	2.9	21.5	22.5	19.5
250 μm	5.1	4.3	21.4	8.3	5.3
200 μm	13.4	15.2	28.1	8.2	4.0
150 μm	29.2	28.8	15.1	1.5	1.0
100 μm	34.8	34.2	4.8	0.3	0.2
63 μm	13.5	12.5	-	-	-
< 63 μm	1.5	2.0	0.2	-	-
$d_{50}/\mu\text{m}$	150	140	260	440	480
< 100 $\mu\text{m}/\%$ by weight	15	14.5	0.2	< 0.1	< 0.1

Table 3 Polymerization tests in 200 dm³ reactor;
85°C, 100 dm³ of diesel oil, 7 kg/hour of ethylene,
Pressure (maximum) 9.5 bar, 36 % by volume of hydrogen in the gas space

Catalyst	n _c ¹⁾ [mmol]	n _{AlR₃} ²⁾ [mmol]	CP ³⁾ [kg/g]	MFI 190/5 ⁴⁾ [g/10']	BD ⁵⁾ [g/cm ³]	d ₅₀ ⁶⁾ [μm]
Op. No. 3.1	2	40	25 ⁷⁾	6.0	0.38	160
Op. No. 3.2	2	40	45 ⁸⁾	6.0	0.38	290

Legend, see Table 1

⁷⁾ Ti content of the catalyst: 0.85 mmol/g

⁸⁾ Ti content of the catalyst: 1.7 mmol/g

Particle size distributions, see Table 2

According to gel permeation measurements these are products having a narrow molecular weight distribution and M_w/M_n values between 4.5 and 5.5

Table 4 Polymerization tests in 200 dm³ reactor;
 85°C, 100 dm³ of diesel oil, 7 kg/hour of ethylene,
 Pressure (maximum) 9.5 bar, 55 % by volume of hydrogen in the gas space

Catalyst	n_c [mmol]	n_{AlR_3} [mmol]	CP [kg/g]	MFI 190/5 [g/10']	BD ⁵⁾ [g/cm ³]	d_{50} [μ m] ⁶⁾
Op. No. 4.1	9	100	10	2.8	0.37	190
Op. No. 4.2	9	100	11	3.0	0.38	210
Op. No. 4.3	9	100	25	4.0	0.35	350

Legend, see Table 1

Difference:

⁸⁾ Co-catalyst: isoprenylaluminum

Table 5 Polymerization tests in 200 dm³ reactor;
 85°C, 100 dm³ of diesel oil, 7 kg/hour of ethylene,
 Pressure (maximum) 9.5 bar, 50 % by volume of hydrogen in the gas space

Catalyst	n_c ¹⁾ [mmol]	n_{AlR_3} ¹⁰⁾ [mmol]	CP ³⁾ [kg/g]	MFI 190/5 ⁴⁾ [g/10']	BD ⁵⁾ [g/cm ³]	d_{50} ⁶⁾ [μ m]
Op. No. 5.1	1.5	25	30	3.0	0.34	150
Op. No. 5.2	1.5	25	30	3.5	0.32	160
Op. No. 5.3	1.0	20	50	4.0	0.30	280
Op. No. 5.4	1.0	20	50	4.5	0.30	290

Legend, see Table 1

Difference:

¹⁰⁾ Co-catalyst: triisobutylaluminum

Table 6 Polymerization tests in 200 dm³ reactor;85°C, 100 dm³ of diesel oil, 5 kg/hour of ethylene,

40 % by volume of hydrogen in the gas space,

Catalyst operation no. 4.3

Comonomer	Volume of comonomer after 5 minutes/dm ³	Volume of comonomer subsequently added/dm ³	n_c [mmol]	n_{ALR} [mmol]	p [bar]	CP [kg/g]	MFI/190/5 [g/10']	d [g/cm ³]	BD [g/cm ³]	d_{50} [μ m]
Propene	0.5	2.9	0.15	120	4	35	1.4	0.935	0.37	390
1-Butene	0.45	1.3	0.15	120	4	33	1.2	0.940	0.35	370
1-Hexene	0.8	4.2	0.20	150	5	36	1.1	0.941	0.35	390
1-Octene	1.1	8.9	0.25	300	6	32	1.2	0.941	0.34	380

Claims

1. A process for the preparation of a poly-1-olefin by polymerizing a 1-olefin of the formula $R^1CH=CH_2$ in which R^1 is hydrogen or an alkyl radical having 1 to 10 carbon atoms, in suspension, in solution or in the gas phase, at a temperature of 20 to 200°C and under a pressure of 0.5 to 50 bar, in the presence of a catalyst composed of the reaction product of a magnesium alcoholate with a transition metal compound (component a) and an organometallic compound of a metal of group I, II or III of the periodic table (component b), which comprises carrying out the polymerization in the presence of a catalyst in which the component a has been prepared by reacting a transition metal compound of titanium, zirconium, vanadium or chromium with a gel-like dispersion of the magnesium alcoholate in an inert, saturated hydrocarbon.
2. The process as claimed in claim 1, wherein a simple magnesium alcoholate of the formula $Mg(OR^1)(OR^2)$ in which R^1 and R^2 are identical or different and are each an alkyl radical having 1 to 6 carbon atoms is employed.
3. The process as claimed in claim 2, wherein the magnesium alcoholate employed is $Mg(OC_2H_5)_2$, $Mg(OnC_3H_7)_2$ or $Mg(OiC_3H_7)_2$.

4. A process as claimed in claim 1, substantially as hereinbefore described and exemplified.

5. A poly-1-olefin whenever prepared by a process claimed in a preceding claim.

Dated this the 31st day of May, 1991

F. R. KELLY & CO.

BY: Margaret O'Sullivan EXECUTIVE

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AGENTS FOR THE APPLICANTS

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